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Investigation of adhesive performances by scanning force microscopy

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Summary

In this work an original investigation of the polymer adhesive properties by scanning force microscopy (SFM) is proposed. Polyethylene terephthalate (PET)/ethylene vinylacetate copolymers (EVA) assemblies have been separated using a peel test. SFM (tapping mode) is used to study the adhesive surface (EVA) after the mechanical separation. The topographic analysis allows to determine the average roughness due to the polymer surface deformation. A tentative correlation between the surface deformation and the adherence force is proposed. The result show that the polymer which possess the higher adhesive strength presents the greater surface deformation, measured on the SFM image. A relatively good correlation between the evolution of the adherence force and the variation of the surface topography analysed by SFM is highlighted in this original work.

Introduction

Traditionally, electron microscopies have been used to examine the topography and structure of polymers films. However, the analysis of polymer surfaces by electron microscopy presents some inconveniences. First, polymers are very sensitive to bombardment-induced damage and chemical and physical changes occur during beam exposure. Second, a sample pre-preparation, for example the deposition of conducting coating, is necessary for most polymers because of their poor electrical conductivity. On the contrary, scanning force microscopy (SFM) offers considerable potential for the surface structures of polymeric materials study, with an improved resolution, and the possibility to investigate local properties (1,2). SFM, and more precisely atomic force microscopy (AFM) allow, for example, the investigation of viscoelastic and rheological properties and surface molecular mobility (3,4,5,6) or the study of microphase domains separation in latex blends and copolymers (7,8). SFM is also fruitful for the characterization of crosslinking density (9), crystalline structure (10) and conformational

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organization (11). SFM is finally a very powerful technique to study surfaces structures from the micron to atomic scale. An other advantage offered by SFM the is the possibility of direct and non-destructive access to the surface topography of polymers surfaces.

In contact mode SFM, the probe tip is mounted on a cantilever and scans over the sample surface, while maintaining a contact with the surface. However, for soft samples such as polymers, the tip-force may induce an irreversible destruction of the surface so that imaging might become impossible. To overcome such problem, tapping mode AFM was developed. In this technique, the cantilever oscillates near its resonance frequency, so that the tip makes contact with the sample only briefly during each oscillation cycle. This imaging mode is one of the most commonly used in oscillatory SFM techniques (8,12) and its operation under small oscillation amplitudes eliminates the lateral forces exerted on the sample surface by the scanning tip. This results in a change of the amplitude, resonance frequency and phase angle of vibration due to the tip/surface interaction.

In this work, we propose an original investigation of the polymer adhesive properties by SFM. Polyethylene terephthalate (PET)/ethylene vinylacetate copolymers (EVA) assemblies have been delaminated using a peel test. The adhesive surface (EVA) has been analysed by SFM (tapping mode) after the mechanical separation. The topographic analysis allows to determine the roughness (8,12,13,14) due to the polymer surface deformation. A tentative correlation between the surface deformation and the adherence force (measured by the peel test) is proposed.

Experimental

Four ethylene-vinyl acetate copolymers have been studied. The vinyl acetate content is the same for all the EVA and is equal to 28 wt%. The copolymers, of various grades, differ by their molecular weight, determined by size exclusion chromatography. Table 1 gives the molecular weight of the different EVA.

Reference	EVA A	EVA B	EVA C	EVA D
Mw (g/mol)	41600	39500	34000	23500

Table 1 : Molecular weight of the EVA copolymers

EVA C contains an additive (process agent, long chain amide) which avoids the agglomeration of the polymer pellets. An other consequence of the presence of this additive in sample C is to increase the adherence level of this polymer.

The substrate used is a 100 μm film of polyethylene terephthalate (PET). PET/EVA/PET assemblies are obtained under press at 150°C. A pressure equal to 1.5 MPa is applied during 5 minutes and a circulating water in the press platens ensures the cooling of the films to room temperature. A thickness of the EVA layer equal to 300 μm is obtained by inserting spacers under the platens.

Peel tests were performed on the assemblies using a tensile test machine (DY34 from MTS). A peel angle of 180° and a peel rate equal to 300 mm/min are used. The peel force, F, is recorded and the peel energy, G, can be calculated using the following equation (15).

$G = F\,(1-\cos\theta)/l$

where l is the width of the assemblies and θ the peel angle.

In our case, θ is equal to 180°, that leads to : $G = 2F/l$.

If F is given in mN and l in mm, G is expressed in mN/mm (i.e. N/m).

The failure surfaces of the EVA adhesives, obtained after the mechanical separation, were investigated by SFM. Tapping mode SFM (Digital Instruments, NanoScope III dimension 3000) allows the drawing of microscopic images of the EVA surfaces. A conic monocrystalline silicon tip is used. The amplitude of the drive signal, that is the amplitude of the drive voltage applied to the piezoelectric crystal that vibrates the cantilever, is equal to about 2 V. A tapping and scanning frequencies were set to 328 KHz and 0.526 Hz respectively. Images were taken under ambient conditions (air and room temperature)

Results

Results of the peel test, performed on the PET/EVA/PET assemblies, are gathered in table 2. In all cases, the rupture is adhesive, i.e. at the PET/EVA interface.

Reference	EVA A	EVA B	EVA C	EVA D
Peel energy [mN/mm]	9 ± 1	6 ± 1	285 ± 1	24 ± 1

Table 2 : Peel energy of EVA/PET assemblies

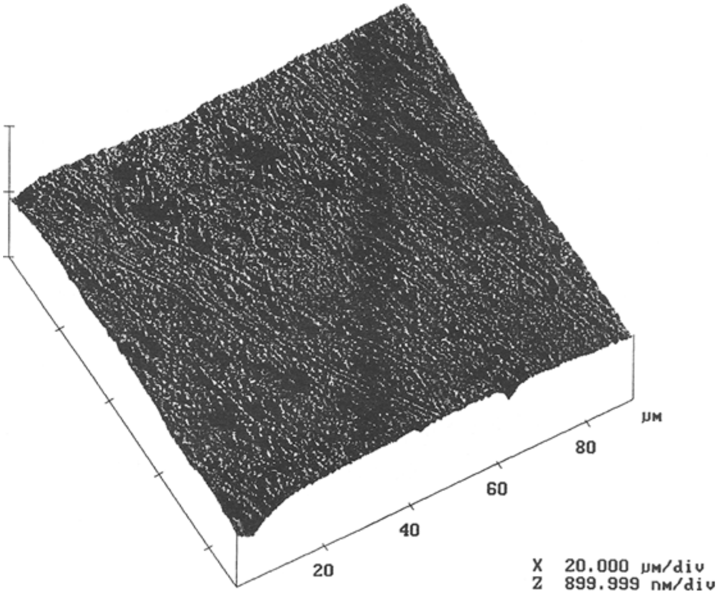

Figure 1 : AFM image of the peeled EVA A surface

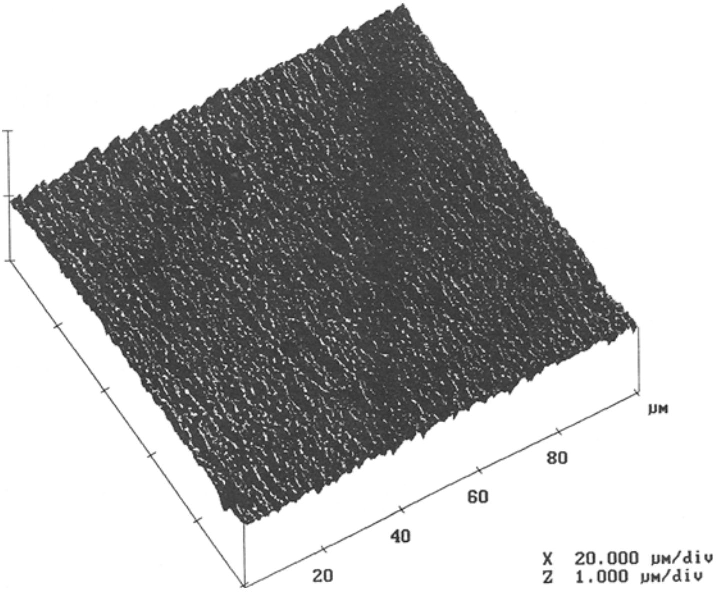

Figure 2 : AFM image of the peeled EVA B surface

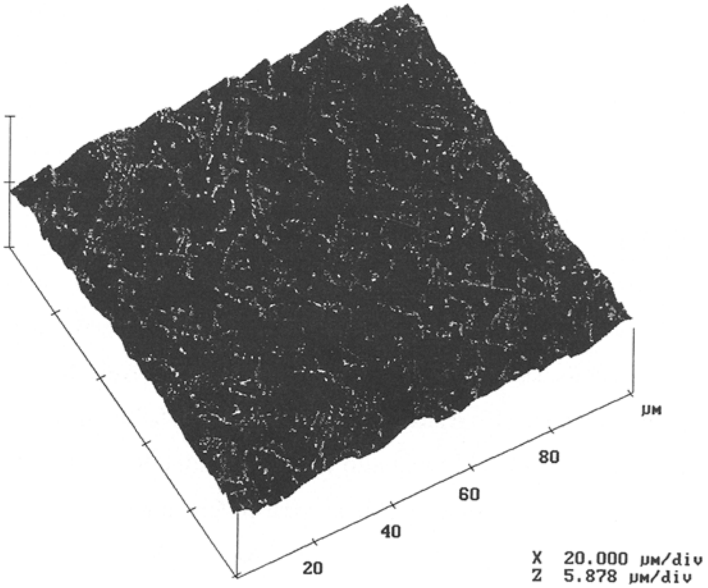

Figure 3 : AFM image of the peeled EVA C surface

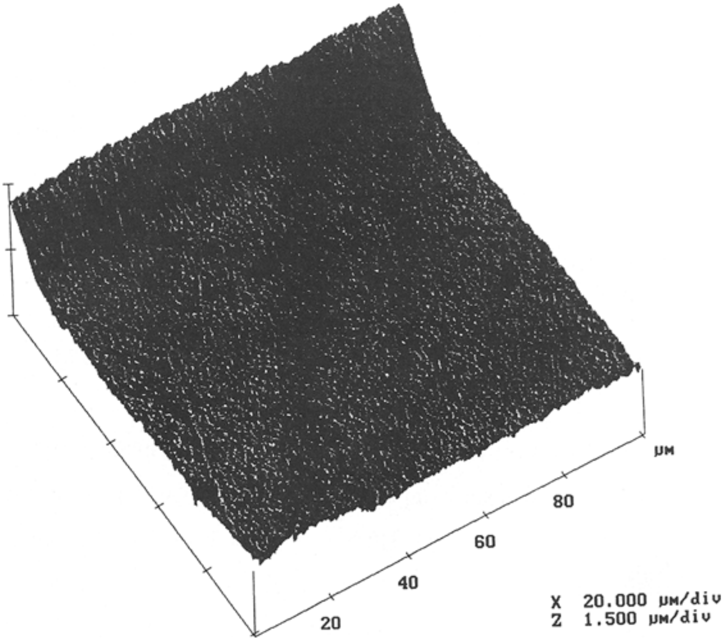

Figure 4 : AFM image of the peeled EVA D surface

It appears that the adherence energy is not identical for all the EVA. Indeed, a higher value is obtained for EVA C, explained by the presence of an additive in this polymer. Interfacial migration of such additive contributes to an increase of the interfacial interactions density. For EVA A and B, a quite similar and low value is obtained, considering the experimental precision. EVA D presents also a lower adherence value compared to EVA C.

Figures 1, 2, 3 and 4 presents the SFM three-dimensional topographic images of the peeled film surfaces of EVA A, B, C and D respectively. These perspective height images are better defined than the surface images using different colour levels. It is necessary to take in account the amplitude of Z scales, which is not identical for all the samples, before compare the AFM images. It is important also to notice that the EVA films are moulded again the same smooth PET substrate, and possess, therefore, a theoretical identical low intrinsic roughness, before the peel test. It can be shown on the AFM images that the peeled surfaces of EVA A, B, and D are relatively smooth, compared to EVA C, for which a tortured relief is observed.

It can be also noted that the EVA B surface is slightly more deformed compared to the EVA A surface. The surface roughness can be quantified using the average roughness, Rz, which corresponds to the average difference in height between the five highest peaks and the five lowest valley relative to the mean plane. The Rz values are directly calculated by the Nanoscope software. In table 3 are given the values of Rz for the different EVA.

Reference	EVA A	EVA B	EVA C	EVA D
Rz [nm]	26	74	236	45

Table 3 : Average roughness Rz of the peeled EVA films measured by AFM

By comparing the peel test results and the SFM images, some evident and interesting correlation can be proposed. Indeed, it appears that the polymer which possess the higher adhesive performances, i.e. EVA C, presents the more deformed surface after the peel test. The surface deformations are induced during the peel test, by the force of separation. For EVA A, B and D, for which a lower adherence is measured, the surface deformation is less pronounced, but EVA B presents a slightly more perturbed surface compared to EVA A, despite the fact that the adherence levels of both EVA A and B are quite similar. It can be concluded that a high adherence level difference is necessary to induce a significant difference in the surface deformation magnitude. For EVA A, B, and D, it is difficult to establish some significant comparisons and conclusions, due to the fact that the surface deformations are close.

However, the one must take into account the polymer films mechanical properties, especially the modulus. EVA differ by their molecular weight and therefore also by their modulus. To a first approximation, it is possible to consider the Young modulus, knowing nevertheless that the peel test involves a more complex deformation. The higher peel force measured for EVA A compared to EVA B can perhaps be explained by the fact that the modulus of EVA A is higher compared to EVA B. A lower surface deformation for EVA A is then induced. It is important however to notice that the observed deformation is a residual plastic deformation and not an elastic deformation. Moreover, a great quantity of the peel energy is dissipated by a viscous process in the adhesive, that can not be reflected by considering the elastic properties only. The use of the Young modulus is therefore not rigorous but allows make a rapid and rough interpretation. For EVA C, the greater deformation is the consequence of a higher adherence force.

Even if the quantification is still actually difficult, AFM technique allows to give a qualitative appreciation and classification of the adhesive according to their adhesive performance.

Further works are necessary, particularly concerning the mechanical approach of this surface deformation. The originality of this study is to demonstrate that the SFM technique can be, in some cases, a fruitful method to investigate an adherence problem by analysing the residual surface deformation, that constitutes an innovative approach.

Conclusion

The study of the adherence performance of some ethylene copolymers both by a peel test and by SFM has shown that the polymer which possess the higher adhesive strength present the greater surface deformation. This latter is evidenced by the important roughness measured on the SFM image. There is therefore a relatively good correlation between the evolution of the adherence force determined by a mechanical test and the the surface topography variation analysed by SFM, at least when the adherence level difference are significant.

Topographic SFM images are also able to allow an evaluation of the adherence, through the measurement of the polymer surface deformation, in the case of an interfacial failure.

This can be of major interest for the study and comparison, for example, of the adherence between a given adhesive and various flat and rigid substrates. An other interest of this approach is the possibility to investigate more precisely the energy loss induced by the deformation of the adhesive layer, in order to approach the ultimate ideal in adhesion science, i.e. the knowing the true value of adhesion from the adherence measurement.

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